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(54) **Polymer composition for injection moulding.**

(57) Capsules and other shaped products formed from a moldable starch composition in an injection molding device is dislosed in the present invention. The composition comprising starch having a molecular mass range of 10,000 to 20,000,000 Dalton, and a water content range from 5 to 30% by weight. The starch contains about 0 to 100% of amylose, and about 100 to 0% of amylo-pectin.

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POLYMER COMPOSITION FOR INJECTION MOULDING

BACKGROUND OF THE INVENTION

A. FIELD OF THE INVENTION

The present invention relates to a moldable starch composition for use in an injection molding device to produce capsules. The present invention utilizes starch made from corn wheat, potatoes, rice, tapioca and the like. Said types of starch have a usual molecular mass range of 10,000 to 20,000,000 Dalton.

The starch contains about 0 to 100% of amylose, and about 100 to 0% of amylo-pectin; preferably 0 to 70% of amylose, and about 95 to 10% of amylo-pectin, and is most preferably potato starch and corn starch.

When in the following description the term "starch" is used, this also includes foams, modifications or derivatives of starch, and combinations thereof with hydrophilic polymer compositions whose properties are acceptable for the intended injection molded products, especially capsule materials.

Hydrophilic polymers are polymers with molecular masses from approximately 10^3 to 10^7 Dalton carrying molecular groups in their backbone and/or in their side chains and capable of forming and/or participating in hydrogen bridges. Such hydrophilic polymers exhibit in their water adsorption isotherm (in the temperature range between approximately 0 to 200 degrees C) and inflection point close to the water activity point at 0.5.

Hydrophilic polymers are distinguished from the group called hydrocolloids by their molecular dispersity of said hydrophilic polymers a fraction of water - according to the working range of the present invention - of 5 to 30% by weight of said hydrophilic polymers must be included provided that the temperature of said hydrophilic polymers is in the working range between 80 degrees C and 240 degrees C of the present invention.

It is a primary object of the present invention to utilize starch compositions in the production of injection molded products, especially capsules.

REFERENCES TO COPENDING PATENT APPLICATIONS

Concurrently with this application please also refer to co-pending European Patent Application No. 83301642.1 filed 24th March 1983 and European Patent Application No. 83301643.9 filed 24th March 1983.

B. DESCRIPTION OF THE PRIOR ART

Capsule-making machines have been developed to utilize dip-molding technology. Such technology involves the dipping of capsule-shaped pins into a gelatin solution, removing the pins from the solution, drying of the gelatin upon the pins, stripping off the gelatin capsule parts from the pins, adjusting for length, cutting, joining and ejecting the capsules. Prior art capsule-making machines have utilized the combination of mechanical and pneumatic elements to perform these functions at speeds up to about 1,200 size 0 capsules per minute. While the above described apparatusses are in general suitable for the intended purposes, it is desirable to produce capsules by injection molding at considerably higher speed, while at the same time precisely controlling the properties of the starch in order to produce the capsules hygenically and with minimum dimensional deviations so that the capsules can be filled on high speed equipment.

A prerequisite for any material to be moldable by an injection process is its ability to pass a glass transition point at a temperature compatible with the thermal stability of the material and the technical possibilities of an injection molding device. A pre-requisite of any material to deliver shaped products of high dimensional stability in an injection

molding process is its minimum elastic recovery after the mold is opened. This can be achieved by setting the dispersity of said material at the molecular level during the injection process.

Shirai et al. in US patent 4,216,240 describes an injection molding process to produce an oriented fibrous protein product. The fibrous product obtained by this process differs fundamentally from the transparent glasslike material of the capsules obtained from the present invention. Furthermore to obtain a flowable mass for the molding process, the protein mixtures used by Shirai et al. have to be denatured and thus lose their capacity to undergo dissolution.

Nakatsuka et al. in US Patent 4,076,846 uses binary mixtures of starch with salts of protein materials to obtain an edible shaped article by an injection molding process. With the present invention shaped articles can be produced with starch without admixture with salts of protein materials therewith.

Heusdens et al. in U.S. Patent No. 3,911,159 discloses the formation of filamentous protein structures to obtain edible products of improved tenderness. With the present invention shaped articles are produced without a filamentous protein structure.

The use of an injection molding device for producing capsules with starch is new and has not been suggested in the technical literature. Many useful products can be prepared by the injection molding of starch other than capsules with the necessity of high form stability and minimum dimensional deviations. These products would include candies, packaging containers for food-stuffs, pharmaceuticals, chemicals, dyestuffs, spices, fertilizing combinations, seeds, cosmetics and agricultural products and matrices of various shapes and size of starch compositions containing substances and/or active ingredients including food stuffs, pharmaceuticals, chemicals,

dyestuffs, spices, fertilizing combinations, seeds, cosmetics and agricultural products, which are micro-dispersed within the matrix and released from it through disintegration and/or dissolution and/or bioerrosion and/or diffusion depending on the solubility characteristics of the used starch composition. Some of these products may also result in a controlled release delivery system for the enclosed substance. Furthermore, medical and surgery products can be prepared by injection molding starch compositions. The biodegradable nature of starch makes it environmentally desirable over certain materials presently being used. In addition, the non-toxic mixture of the materials further enhances their desirability as a material to be used in the injection molding industry. It is an object of this invention to encompass all injection molded products that may be produced by the teachings of that invention. The present invention distinguishes from the known prior art described above, by the recognition that starch possesses a dissolution point within a temperature range usable for an injection molding process, provided the water content of the starch lies within a characteristic range, giving allowance to avoid any essential drying or humidification processes of the capsules. Above the dissolution point the starch is in the state of molecular dispersity. Due to the present invention the starch during the injection molding process is for a considerable time at a temperature which is higher than the temperature of the dissolution point. When materials, such as medicaments, food-stuffs, etc. are dispersed in the starch compositions, quantities can not be employed that will so effect the properties of the starch that it will no longer be injection moldable.

SUMMARY OF THE INVENTION

The present invention covers an improved starch composition for use in an improved automatic injection

molding device to control the optimum time, temperature pressure and water content of the composition in formed and shaped parts and objects molded from said composition. The starch has a molecular mass range of 10,000 to 20,000,000 Dalton.

The starch composition has a water content range of approximately 5 to 30% by weight.

The starch contains about 0 to 100% of amylose, and about 100 to 0% of amylo-pectin.

It is therefore a primary object of the present invention to provide a new and improved moldable composition of starch for use with an injection molding apparatus which alleviates one or more of the above described disadvantages of the prior art compositions.

It is a further object of the present invention to provide an improved moldable composition of starch for use with an injection molding apparatus in a method of molding capsules at high speed and with precision in order to use the capsules with high speed filling equipment.

It is a still further object of this invention to provide useful injection molded products, especially capsules, and a process for preparing said injection molded products.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention both as to its organization and method of operation together with further objects and advantages thereof will best be understood by reference to the following specifications and taken in conjunction with the accompanying drawings.

Fig. 1 is a schematic layout of a reciprocating screw injection molding device for making capsule parts;

Fig. 2 is a schematic of an injection molding

work cycle for making capsule parts;

Fig. 3 is a schematic of an embodiment of a combined injection molding device-microprocessor apparatus for capsule parts;

Fig. 4 is an expanded schematic of the exit end of the injection molding device;

Fig. 5 is the diagram of dependence of shear viscosity of starch within the pertinent ranges of the shear rate in the present invention;

Fig. 6 is the diagram of molding area for starch within the ranges of temperature and pressure of starch for the present invention;

Fig. 7 is the diagram of dependence of glass transition temperature range and melting temperature range for the pertinent water content ranges of starch;

Fig. 8 is the diagram of dependence of differential calorimeter scan in which the heat consumption rate of the starch is plotted for the pertinent temperature range of the present invention; and

Fig. 9 is a diagram of dependence of equilibrium water content of the starch in the water activity program.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to Fig. 1 the injection molding device 27 generally consists of three units: a hopper unit 5, an injection unit 1 and a molding unit 2.

The function of the hopper unit 5 is receiving, storing, maintaining and feeding starch 4 at a constant temperature and at a constant water content. The hopper unit 5 comprises a vertical cylinder 30 having a closed top 31 with an inlet 32 therein to receive starch 4. At the bottom of the vertical cylinder 30 is a closed conical funnel 33 and a discharge outlet 34 to feed starch 4 into an inlet 34 of the injection unit 1. There is an air duct 35 communicating between the closed top 31 and the conical funnel 33 wherein air is

circulated by a blower 36, the air temperature is maintained by a thyristor 37 and the air relative humidity is maintained by a steam injector 38.

The function of the injection unit 1 is melting, dissolving in water, and plasticizing in the extruder barrel 17 the starch 4 fed from the hopper unit 5 into the extruder inlet 54 and injecting the plasticized starch 14 into the molding unit 2.

The function of the molding unit 2 is automatically holding, opening and closing the mold 6 having capsule shaped cavities 19 therein, and ejecting the capsule parts 7 therefrom.

Within the injection unit 1 the screw 8 both rotates and undergoes axial reciprocal motion. When the screw 8 rotates, it performs the functions of melting, dissolving in water, and plasticizing the starch 4. When the screw 8 moves axially, it performs the function of injecting by transporting and ramming the plasticized starch 14 into the mold 6. The screw 8 is rotated by a variable-speed hydraulic motor 9 and drive 10, and its axial motion is reciprocated by a duplex hydraulic cylinder 11.

Compression of the plasticized starch 14 in front of the rotating screw 8 forces back the screw assembly 20 containing the screw 8, the drive 10 and the motor 9. When the screw assembly 20 reaches a preset back position a limit switch 12 is contacted. When a defined time has elapsed during which the starch 4 becomes fully plasticized starch 14 the hydraulic cylinder 11 brings the screw assembly 20 forward and uses the screw 8 as a ram for the plasticized starch 14 to be injected through a valve body assembly 50 including a one-way valve 15, a needle valve 23, nozzle 22 and an outlet port 21 into the molding unit 2. The one-way valve 15 prevents the plasticized starch 14 from going back over the helical flutes 16 of the screw

8. The extruder barrel 17 has heating coils 18 to heat the starch 4 while it is being compressed by the screw 8 into plasticized starch 14. It is desirable for the plasticized starch 14 to be heated at the lowest possible temperature and to be transported with the lowest possible speed of the screw 8. The speed of the screw 8 and the heating of the plasticized starch 14 within the extruder barrel 17 by the steam heating coils 18 control the quality and the output rate of the plasticized starch 14 injected into the molding unit 2. The molding unit 2 holds the mold 6 having capsule shaped cavities 19 into which the plasticized starch 14 is injected and maintained under pressure. Refrigerant cooling conduits 24 encircle the mold 6 so that when the plasticized starch 14 in the mold 6 has cooled and sufficiently solidified, the molding unit 2 opens, the mold 6 separates and the capsule parts 7 are ejected.

Referring now to Fig. 1 and also to Fig. 2 which depicts the injection molding work cycle for starch 4 containing approximately 20% water, by weight. In general the work cycle of starch 4 is as follows in the injection molding device 27 of the present invention:

a. starch 4 is fed into the hopper unit 5 where it is received, stored and maintained under conditions of temperature ranging from ambient to 100°C, pressure ranging from 1-5 x 10^5 Newtons per square meter ($N \times m^{-2}$) and water content ranging from 5 to 30% by weight of starch

b. the stored starch 4 is melted under controlled condition of temperature ranging from 80 to 240°C, water content ranging from 5 to 30% by weight of starch and pressure ranging from 600 to 3000 x 10^5 $N \times m^{-2}$,

c. the molten starch 4 is dissolved in water under controlled conditions of temperature ranging from 80 to 240°C pressures ranging from 600 to 3000 x 10^5 N x

m^{-2} and water content ranging from 5 to 30% by weight of starch.

d. the dissolved starch 4 is plasticized under controlled conditions of temperature ranging from 80 to 240°C, pressure ranging from 600 to 3000 x 10^5 N x m^{-2} and water content ranging from 5 to 30% by weight of starch.

e. the plasticized starch 14 is injected into the mold 6 under controlled conditions of temperature above 80°C, injection pressure ranging from 600 to 3000 x 10^5 N x m^{-2} and a clamping force of the mold 6 with a range of approximately 100 to 10,000 Kilo Newton, and

f. the capsule-shaped parts 7 are ejected from the plasticized starch 14 within the mold 6.

Beginning at point A of Fig. 2 the screw 8 moves forward and fills the mold 6 with plasticized starch 14 until Point B and maintains the injected plasticized starch 14 under high pressure, during what is called the hold time from point B until Point C of Fig. 2. At Point A the one-way valve 15 at the end of the screw 8 prevents the plasticized starch 14 from flowing back from the cylindrical space in front of the screw 8 into the helical flutes of screw 8. During hold time, additional plasticized starch 14 is injected, offsetting contraction due to cooling and solidification of the plasticized starch 14. Later, the outlet port 21, which is a narrow entrance to the molding unit 2 closes, thus isolating the molding unit 2 from the injection unit 1. The plasticized starch 14 within the mold 6 is still at high pressure. As the plasticized starch 14 cools and solidifies, pressure drops to a level that is high enough to ensure the absence of sinkmarks, but not so high that it becomes difficult to remove the capsule parts 7 from the capsule-shaped cavities 19 within the mold 6. After the outlet port 21 closes, at Point C, screw 8 rotation commences. The

plasticized starch 14 is accommodated in the increased cylindrical space in front of the screw 8 created by its backward axial motion until Point D. The flow rate of the plasticized starch 14 is controlled by the speed of the screw 8 and the pressure is controlled by the back pressure (i.e., the hydraulic pressure exerted on the screw assembly 20) which in turn determines the pressure in the plasticized starch 14 in front of the screw 8. After plasticized starch 14 generation for the next shot into the mold 6, the screw 8 rotation ceases at Point D. The starch 4 on the stationary screw 8 is held at melt temperature from Points D to E by heat conduction from the heating coils 18 on the extruder barrel 17. Meanwhile, the solidified capsule parts 7 are ejected from the mold 6. Thereafter, the mold 6 closes to accept the next shot of plasticized starch 14. All of these operations are automated and controlled by a microprocessor as hereinafter described.

Referring now to Fig. 2 and and also to Fig. 3. The injection molding work cycle of Fig. 2 is accomplished on the injection molding device 27 of Fig. 3 by hydraulic and electrical components and the corresponding circuits controlled by the microprocessor 28 of Fig. 3.

Through the use of solid-state circuitry and of speed, temperature, limit and pressure switches for the electric and hydraulic systems, the microprocessor 28 of the present invention utilized command signals in its memory 51 for the parameters of time, temperature and pressure conditions of Table 1 below for the injection molding work cycle of Fig. 2 to be accomplished by the injection molding device of Fig. 3 for producing capsule parts 7.

TABLE 1

Ranges of Time, Temperature and Pressure at the top of the Screw for the Injection Molding Work Cycle of Fig.2:

	POINTS				
	A	B	C	D	E
Time (seconds)	10^{-2} -1	10^{-2} -1	10^{-2} -1	10^{-2} -1	10^{-2} -1
Temperature (°Celsius)	ambient-100	80-240	80-190	80-240	80-240
Pressure	A - B	B - C	C - D	D - E	
(10^5 X N x m^{-2})	600-3000	600-3000	10-1000	10-1000	

(Newtons per square meter)

Referring now to Fig. 3 illustrating the combined injection molding device 27 and microprocessor 28 utilizing the method of present invention.

The combined injection molding device 27 and microprocessor 28 comprises six control circuits of which five are closed-loop, fully analog, and one is on-off. Starting at molding cycle Point A in Fig. 2, the injection molding work cycle operates as follows:

When sufficient plasticized starch 14 has accumulated in front of the screw 8 (microprocessor limit switch controlled) and also when the screw assembly 20 carrying the screw 8, drive 9 and hydraulic motor 11 has been pushed far enough backwards against a constant back-pressure as controlled by control circuit 2, limit switch 12 will be actuated by position sensing circuit I4. The two conditions for actuating cylinder 11 (barrel unit forward) are: 1) clamping force of the mold is built-up, and 2) limit switch 12 is activated. This rams the barrel 17 together with the nozzle 14 with screw assembly 20 forward, thus for sealing purposes. Sufficient pressure is controlled by control circuit 2 with means of pressure sensor I_2. Under

these conditions hydraulic piston 9 rams the screw assembly 20 forward, thus injecting the plasticized starch 14 into the mold 6 when molding cycle Point B of Fig. 2 is reached, and, as controlled by the microprocessor 28, the screw 8 remains for a certain period of time until Point C stationary in this forward position under high pressure.

From molding cycle Point B of Fig. 2 onwards the plasticized starch 14 cools down in the mold 6 and the port 21 closes at molding cycle Point C of Fig. 2.

At molding cycle Point C of Fig. 2 the screw 8 starts to rotate again and the hydraulic pressure reduces from holding presure to back pressure in the hydraulic cylinder 11. This pressure set is less than the holding pressure at Point C.

The barrel 17 is kept under constant pressure towards the mold 6 by the pressure in the back position of the hydraulic cylinder 11. This is achieved by means of the control circuit 2 where a proportional hydraulic valve is controlled by a pressure sensor circuit I_2.

As the screw 8 rotates a recharge of starch 4 is made from the hopper 5. During a certain time period and at a defined rotating speed of the screw 8, controlled by control circuit 3, a precise amount of starch 4 is fed into the extruder barrel 17. Control circuit 3 is actuated by speed sensor circuit I_3, measuring the rotating speed of the screw 8 and sensing back to a hydraulic proportional flow control valve 0_3 controlled by control circuit 3, thus assuring a constant rotating speed of the hydraulic motor 10, irrespective of the changing torque resulting from introduction of the starch 4 recharge.

When the load time is completed, the screw 8 rotation is stopped and molding cycle Point D of Fig. 2 is reached. The time from molding cycle Points D to A

of Fig. 2 allows for the starch 4 to plasticize completely under controlled temperature conditions as controlled by control circuit 1.

A temperature sensor circuit I_1 senses a thyristor heat regulator O_1 heating the extruder barrel 17 as directed by control circuit 1.

During the time interval from molding cycle Points B to E on Fig. 2, the mold 6 has cooled down sufficiently so that the finished capsule parts 7 can be ejected from the mold 6.

After ejection of the capsule parts 7, the work cycle returns to Point A of Fig. 2 where a certain volume of plasticized starch 14 has accumulated in front of the screw 8 (sensing circuit I_4 is actuated and time has elapsed) so that the work cycle of Fig. 2 can be repeated.

It is important to note the temperature and humidity control loops 5 and 6, for the maintenance of precise water content of the starch 4 in the hopper 5, which is essential for proper operation at the desired speeds.

The microprocessor 28 includes a memory section 51 to store the desired operating parameters; a sensing and signaling section 52 to receive the sensing signals of actual operating conditions, to detect the deviation between the desired and actual operating conditions, and to send signals for adjustment through the actuating section 53 to the thyristors and valves.

Referring now to Fig. 4 there is shown the valve assembly 50 including the outlet port 21, the nozzle 22, the needle valve 23, and the bearing 15. These elements operate as follows:

At Point A in Fig. 2 the needle valve 23 is retracted from the outlet port 21 when the pressure in the starch 14 while the bearing 15 is pressed against the valve body so as to form an inlet opening

55 for plasticized starch 14 into the nozzle 22 which defines a charging chamber for plasticized starch 14. The plasticized starch 14 is injected through nozzle 22 and into the mold 6 during the mold-filling time between Points A and B in Fig. 2. At Point C in Fig. 2 the needle valve 23 is pushed forward so as to close the outlet port 21 during which time between Point C and E in Fig. 2, the inlet of mold 6 is closed and the capsule part 7 in the mold 6 is cooling. The needle valve 23 remains closed between Point E and A in Fig. 2 during which time the capsule part 7 is ejected from the mold 6.

The one-way valve 15 and the needle valve 23 are actuated by a spring-tensioned lever 25 which normally closes both the outlet port 21 and the nozzle 22 until the lever 25 is cam-actuated pursuant to signals from the microprocessor 28.

The thermomechanical properties of starch, i.e. storage and loss shear modules at different temperatures, are strongly dependent on its water content. The capsule molding process of the present invention can be used for starch with a water content preferably within a range of 5 to 30%. The lower limit is defined by the maximum processing temperature of 240°C, which in turn cannot be exceeded in order to avoid degradation. The upper limit is determined by the stickiness and distortion of the finished capsules. It should also be noted that plasticizing is caused by heat and pressure when dealing with thermoplastic materials. However, with starch, it is also necessary to have strong shearing forces.

The abbreviations in Table 2 below will be used hereinafter in this application:

Table 2

Abbreviations for Physical Parameters

ABBREVIATION	UNIT	DESCRIPTION
T_a, P_a	Degree C, N x m^{-2}	Ambient temperature and pressure.
H(T,P)	KJoule x Kg^{-2}	Enthalpy of starch-water system at a temperature.
K(T,P)	N^{-1} x m^2	Compressibility of the starch at a given temperature and pressure. Its numerical value is the relative volume change due to change of pressure by a unit amount.
(T,P)	$(\text{Degree C})^{-1}$	Volumetric thermal expansion coefficient of the starch at a given temperature and pressure. Its numerical value is the relative volume change due to change of temperature by a unit amount.
V(g ,T,P)	Kg x sec^{-1}	is the flow rate of the starch at a given temperature and shear deformation rate [sec. $^{-1}$] and pressure. Its numerical value is the volume of a melt leaving the exit cross-sectional area of an injection molding

		device in unit time due to the applied shear deformation rate.
T_{G1}; T_{G2}	Deg C	The temperature range of the glass-transition of the starch.
T_{M1}; T_{M2}	Deg C	The temperature range of the melting of the partially crystalline starch.
T_M		Melting temperature
$T_n(t)$	Deg C	The temperature of the starch in the nozzle area of the injection unit.
$T_t(t)$	Deg C	The temperature of the starch in the mold.
P_t	$N \times m^{-2}$	The pressure of the starch in the mold.
P_n	$N \times m^{-2}$	The pressure in the nozzle area of the starch.
X		The water content of the starch, expressed as the weight fraction of the water - starch system.

For the control and regulation of the injection molding process (IMP) we need knowledge of the

(1) heat consumption of the melting process:

$$H(T_n, P_n) - H(T_a, P_a)$$

(2) the heating rates of the starch in the injection molding device. To calculate this we need the heat conduction number of the starch and the heat transfer number of the starch and the specific material of construction of the barrel which is in contact with the starch.

The heating rate and the heat consumption of the starch give the minimum time interval necessary to make the starch ready to inject and the necessary heating power of the injection molding device.

(3) the T_n depends on X of the starch. If the water content of the starch in the mold is too low, the resulting T_n will be too high and cause degradation. A minimum water content of 5% by weight is required to keep T_n below 240°C.

(4) the flow rate V(g,T,P) is as well strongly dependent on the water content of the starch. To speed up the IMP we need a high flow rate V(g,T,P) which can be achieved by a higher water content.

The upper limit of the water content is defined by the stickiness and mechanical failure of the capsules; a water content of 0.30 cannot be generally exceeded.

The starch in the mold will reduce its volume due to the temperature change T_t-T_a. This would result in voids and diminution of size of the capsule, which therefore would be of unacceptable quality. It is an important requirement in capsule making that the dimensional deviations are less than 1%. To compensate for shrinking by the temperature change, the mold must be filled at a distinct pressure P_n. This filling pressure is determined by the quantities (T,P) and K(T,P). The injection pressure (P_n) depends again on T_n, which as was shown already is in turn strongly dependent on X.

Referring now to Fig. 5, the shear rate dependent shear viscosity of starch at 130 degrees C is shown for starch with a water content X of 0.2.

Referring now to Fig. 6, the molding area diagram for starch with water content of 0.24. During injection

molding the plasticized starch is discontinuously extruded and immediately cooled in a mold of the desired shape of the capsule part. Moldability depends on the starch properties and the process conditions, of which the thermomechanical properties of the starch as well as the geometry and the temperature and pressure conditions of the mold are the most important. In the molding area diagram of Fig. 6 the limits of pressure and temperature are indicated for the processing of starch in the combined injection molder-microprocessor of the present invention. The maximum temperature of 240°C is determined by visible degradation of the starch above that limit. The lower temperature limit of 80°C was determined by the development of too high viscosity and melt elasticity in the preferred water content range X: 0.05 to 0.30. The higher pressure limits of $3x10^8$ N x m^{-2} are given by the start of flashing when the melted starch flows in a gap between the various metal dies which make up the molds, thus creating thin webs attached to the molded starch capsule parts at the separating lines. The lower pressure limits of about $6x10^7$ N x m^{-2} are determined by short shots, when the mold cannot be completely filled by the starch. Shown below in Table 3 are the working parameters for the injection molding process using the starch composition of the present invention.

Table 3

WORKING PARAMETERS FOR INJECTION MOLDING PROCESS

Density	$1.5 - \times 10^3 kg \times m^{-3}$
Cristallinity	20 to 70%
$H(T_n, P_n) - H(T_a, P_a)$	63 KJoule $\times\ kg^{-1}$
Net heating performance for 10 kgs. melt/h (corresponding to 10^6 capsules/h)	6.3×10^2 KJoule
(T_a, P_a)	3.1×10^{-4} (Degree° C)$^{-1}$
Contraction due to crystallization	negligible
Critical shear deformation rate	$10^4 - 10^6$ sec $^{-1}$

The starch compositions of the present invention are extruded and molded as described below:

Referring now to Fig. 7 the glass transition range and the melting temperature range is shown as a function of the composition of the starch-water system. The melting range is very broad with over 100°C in comparison with the melting range of e.g. gelatin, which comes to about 20°C. At temperatures below the glass transition range, ordinary starch, as available commercially, is a partially crystalline polymer containing approximately 30-100% amorphous and approximately 0-70% crystalline parts by volume.

By raising the temperature of said starch at a distinct water content the starch passes through the glass transition range.

Referring again to Fig. 1 said heating process of the starch will take place within the extruder barrel 17. Referring again to Fig. 2 said heating process of the starch will take place during the entire injection molding work cycle. The area in Fig. 7 between the

glass transition range and the melting range is called area II. In area II we find crystalline starch and a starch melt. The glass-transition is not a thermodynamic transition range of any order but is characterized by a change of the molecular movement of the starch molecules and by a change of the bulk storage module of the amorphous starch by several orders of magnitude. By passing from area II to area I in Fig. 7 the translational movements of the starch molecules or those of large parts of said molecules will be frozen in the glass transition temperature range and this is reflected by a change in the specific heat (c_p) and the volumetric thermal expansion coefficient ( ) in said temperature range. By passing from area II to area III due to crossing the melting range of the crystalline starch the helically ordered part of the starch will melt. Referring to Fig. 1 said heating process of the starch will take place within the extruder barrel 17. Referring again to Fig. 2, said heating process of the starch will take place during the entire injection molding work cycle. Said helix-coil transition is a true thermodynamic transition of the first order and is an endothermic process. Said transitions can be detected by scanning calorimetry or by measurement of the change of the linear viscoelastic bulk storage module due to change of the temperature. A typical plot of a temperature scan with a differential calorimeter is shown in Fig. 8. On the ordinate is plotted the velocity of the heat consumed by the sample relative to a reference (empty sample holder). The velocity of heat consumption of the sample is due to the change of the temperature of the starch sample, and said temperature is plotted on the abscissa as degrees of Celsius. The base line shift on said plot is corresponding to the glass transition and the peak to the melting or to the helix-coil transition. The linear viscoelastic bulk storage

module E can be measured at small sinusoidal shear deformations of the starch sample.

Referring again to Fig. 1 the heating of the starch 4 to a temperature higher than T_M takes place in the forward part of the extruder barrel 17. Said heating process will be maintained not only by the heating coils 18 but to an important proportion by the internal friction during the screw rotation and the injection process due to the high deformational rates. It was found that the reversible elastic deformation of the injection molded starch 14 after opening the mold 6 is negligible if the temperature of the plasticized starch 14 during the injection process is higher than T_M, otherwise the molding sequence would drop by at least an order of magnitude.

Referring again to Fig. 2 the necessary cooling period for the plasticized starch in the molds - to prevent any reversible elastic deformation of said starch will take place between points B and E of the working cycle. A restriction of the molding sequence to low speed coupled with long keeping of the starch in the mold is undesirable because of two reasons: low output of the product and loss of water content of the starch in the extruder. At the elevated injection temperature there is always a transport of water from the hot to the cold starch in the extruder barrel. Said water transport can be compensated due to the transport of the starch by the screw in the opposite direction.

Referring again to Fig. 1 said transport of starch 4 will be maintained by screw 8. Referring again to Fig. 2 said transport of starch will take place between the points C and D of the working cycle. To build up a stationary water content of the starch in the melting area of the extruder barrel, it is necessary to work at an injection sequence which is

short. To establish a constant and high enough water content of the starch in the extruder barrel, it is further necessary to use starch with the proper shape of the sorption isotherm. (See Fig. 9.) The constant water content of the starch in the extruder barrel is necessary due to the maintenance of constant production conditions. The water content of the starch during the injection must fulfill the condition: X higher than 0.05 otherwise T_M is also higher than 240°C and this is undesirable due to degradation of the starch.

In the procedure of branching and crosslinking of starch, it is important to add crosslinking agents, especially the covalent crosslinking agents, shortly before injection of the molten starch.

Referring again to Fig. 1, an aqueous solution of crosslinking agents is injected in front of a mixing system being placed between barrel 17 and nozzle 15. Referring now to Fig. 4, this device is integrated in the valve body 50. For example, the crosslinking reaction mainly occurs during the injection cycle and the time after ejection of the capsule. By the above described technology on branching and crosslinking there is no disadvantage of changing the thermo-mechanical properties of the starch polymers during the melting and solution process.

The starch compositions are extruded and injected under the following conditions given in Table 4 below:

Table 4

Injection and Molding Conditions for Starch

Injection Unit

Screw diameter	mm	24	28	32	18
Injection pressure	$N \times m^{-2}$	2.2×10^8	1.6×10^8	$1. \times 10^8$	
Calcuted injection	cm^3	38	51.7	67.	21.3
Effective screw length	L:D	18.8	16.1	13.	18
Plasticising capacity (PS)	kg/h(max.)	la) 13.5	21.2	21.	
		lla) 9.2	14.5	15	
		lb) 23.6	34	36	
		llb) 17.5	27	27.	
Screw stroke	mm (max.)	84	84	84	84
Injection capacity	kW	30	30	30	
Injection velocity	mm/s(max.)	2000	2000	2000	2000
Nozzle contact force	kN	41.2	41.2	41.2	41.2
Screw rotating speed	min^{-1}	Var. la)	20	- 80	
		lla)	20	- 17	
		Var. lb)	20	- 60	
		llb)	20	- 40	
Number of heating zones		5	5	5	5
Installed heating capacity	kW	6.1	6.1	6.	
Molding unit					
Clamping force	kN			60	

While the preferred embodiment of the injection molding apparatus is for the method of producing starch capsules from various types of starch, it has been found that quality capsules may also be manufactured utilizing the present invention with starch modified by

a) crosslinking agents as:
   epichlorohydrin, anhydride of dicarboxylic acid, formaldehyde, phosphorous oxychlorine, metaphosphate, acrolein, organic divinylsulfons and the like.

b) crosslinking the starch with microwaves and the like.

c) prior processing like treatment with acids and/or enzymes in order to yield dextrines and/or pregelatinizing and/or treatment with ultrasonic and/or treatment with gamma radiation.

d) Chemical derivations as: oxydized starch, starch monophosphate, starch diphosphate, starch acetate, starch sulfate, starch hydroxyethylether, carboxymethyl starch, starch ether, 2-hydroxypropyl starch, alphatized starch, starch xanthide, starch chloroacetic acid, starch ester, formaldehyde starch, sodium carboxymethyl starch; and

e) mixtures or combinations of these modified starches and starch modification procedures a) to d) respectively.

In addition it has been found that the injection moulding apparatus of the present invention can produce quality capsules with various types of starch and/or with the above mentioned modified starches a), b), c), d) and e) combined with extenders, for example, sunflower proteins, soy-bean proteins, cotton seed proteins, peanut proteins, blood proteins, egg proteins, rape seed proteins and acetylated derivatives thereof; gelatin, crosslinked gelatin, vinylacetate; polysaccharides as cellulose, methylcellulose, hydroxypropyl cellulose, hydroxypropyl-methylcellulose, hydroxymethylcellulose, hydroxyethylcellulose, sodium carboxy methylcellulose, polyvinyl pyrrolidine, bentonite, agar-agar, gum arabic, guar, dextran, chitin, polymaltose, polyfructose, pectin, alginates or alginic acids; monosaccharides, for example, flucose, fructose or saccharose; oligosaccharises, for example, lactose; silicates, carbonates and bicarbonates. The quantity of extender is controlled so as not to effect the ability of the starch to be injection moulded.

In addition it has been found that the injection moulding apparatus of the present invention can produce capsules having enteric properties (2 hours resistant in gastric juice, well soluble within 30 minutes in intestinal juice) with various types of starch and/or with the above mentioned modified starches a), b), c), d) and e) combined with enteric polymers, for example hydroxypropylmethylcellulose phtalate (HPMCP), cellulose acetylphtalate (CAP), acrylates and methacrylates, polyvinyl-acetate-phtalate (PVAP), phtalated gelatin, succinated gelatin, crotonic acid or shellac. The quantity of extender is controlled so as not to effect the ability of the starch to be injection moulded.

For the manufacturing of capsules with different types of starches and/or modified starches and/or extended starches as mentioned above, the utilization of plasticizers, lubricants and coloring agents specifically of pharmaceutical grades leads to optimal product qualities:

Pharmacologically acceptable plasticizers, such as polyethylene glycol or preferably low-molecular weight organic plasticizers, like glycerol, sorbitol, dioctyl-sodium sulfosuccinate, triethyl citrate, tributyl citrate, 1,2-propylenglycol, mono-, di-, tri-acetates of glycerol etc. are utilized at various concentrations of about 0.5 - 40% preferably at 0.5-10% based upon the weight of the starch composition.

Pharmacologically acceptable lubricants, such as lipids, i.e. glycerides (oils and fats), wax and phospholipids, such as unsaturated and saturated plant fatty acids and salts thereof, such as the stearates of aluminum, calcium, magnesium and tin; as well as talc, silicones, etc. are to be used at concentrations of about 0.001 - 10% based upon the weight of the starch composition.

Pharmaceutically acceptable coloring agents, such as azo-dyes and other dyestuffs and pigments as iron oxides, titanium dioxides, natural dyes etc. are used at concentrations of about 0.001 - 10% preferably at

0.001 - 5% based upon the weight of the starch composition.

Examples

To test the method and appratus as decribed before according to the present invention, batches of commercially available native starch with different water contents and extenders were prepared and conditioned and then tested in an injection molding machine at different working conditions.

Referring to Fig. 2 the cycle times of the injection molding-microprocessor apparatus are as follows:

Cycle Points	Times
A-B	1 second, variable, depending on temperature
B-C	1 second
C-D	1 second
D-E	Variable depending on temperature
E-A	1 second

Pressure in the nozzle: $2x10^8 N \times m^{-2}$

Temperatures at different points of screw: (variable, see Examples below.)

In the following Examples the abbreviations mean:

T_b	temperature at beginning of screw (°C)	
T_m	temperature at middle of screw (°C)	
T_e	temperature at end of screw (°C)	
T_n	temperature at nozzle (°C)	
LFV	linear flow velocity (mm/second)	
L	flow length	(cm.)
D	film thickness	(cm.)

Acceptable starch capsules were processed according to the starch compositions and to the working conditions tabulated in the Examples below:

Example 1

Starch composition:

Wheat starch, gelatin 150B, water: 8.2% bw, 73.8 bw, 18bw,

Working condition:

number	T_b	T_m	T_e	T_n	$\frac{L}{D}$	LFV
765	125	130	140	140	66	1000

Example 2

Starch composition:

Wheat starch, gelatin 150B, water: 41% bw, 41% bw, 18% bw

Working conditions:

number	T_b	T_m	T_e	T_n	$\frac{L}{D}$	LFV
126S	125	135	140	140	66	820

Example 3

Starch composition:

Wheat starch, gelatin 150B, water: 67.6% bw, 24.6% bw, 15.8% bw

Working conditions:

number	T_b	T_m	T_e	T_n	$\frac{L}{D}$	LFV
298S	125	135	140	140	66	1200

Example 4

Starch composition:

Wheat starch, water: 79.4% bw, 20.6% bw

Working conditions:

number	T_b	T_m	T_e	T_n	$\frac{L}{D}$	LFV
305S	115	130	140	140	66	820

Example 5

Starch composition:

Wheat starch, water, erythrosine: 78.32% bw, 21.6% bw, 0.0078% bw

Working conditions:

number	T_b	T_m	T_e	T_n	$\frac{L}{D}$	LFV
349S	110	125	135	135	66	1000

Example 6

Starch composition:

Wheat starch, HPCMP, lubricants + plasticizers, water: 9.2% bw, 74.1% bw, 5.1% bw, 7.5% bw

Working conditions:

number	T_b	T_m	T_e	T_n	$\frac{L}{D}$	LFV
349S	110	125	135	135	66	1000

This starch composition yielded an enteric capsule.

Example 7

Starch composition:

Wheat starch, water: 78.5% bw, 21.5% bw

Working conditions:

number	T_b	T_m	T_e	T_n	$\frac{L}{D}$	LFV
400S	130	150	160	160	66	820
404S	110	115	125	125	66	820

Example 8

Starch composition:

Wheat starch, water: 87.3% bw, 12.7% bw

Working conditions:

number	T_b	T_m	T_e	T_n	$\frac{L}{D}$	LFV
405S	150	160	170	170	66	820

Example 9

Starch composition:

Wheat starch, Calcium-stearate, water: 76.8% bw, 3% bw, 20.2% bw

Working conditions:

number	T_b	T_m	T_e	T_n	$\frac{L}{D}$	LFV
411S	100	110	135	135	66	880
413S	130	140	160	160	66	820

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Example 10

Starch composition:

Wheat starch, glycerin, water: 77.2% bw, 3% bw, 19.8% bw

Working conditions:

number	T_b	T_m	T_e	T_n	$\frac{L}{D}$	LFV
410S	100	110	130	130	66	860
414S	130	140	160	160	66	840

Example 11

Starch composition:

Wheat starch, Polyethylene-glycol (10,000 m.w.), water, talcum: 72.5% bw, 3% bw, 22.5% bw, 2% bw

Working conditions:

number	T_b	T_m	T_e	T_n	$\frac{L}{D}$	LFV
412S	100	110	130	130	66	840
415S	130	140	160	160	66	840

Example 12

Starch composition:

Potato starch, water: 80.7% bw, 19.3% bw

Working conditions:

number	T_b	T_m	T_e	T_n	$\frac{L}{D}$	LFV
417S	100	110	130	130	66	840

Example 13

This example demonstrated the dependence of the capsules disintegration properties on the content of amylose. For these tests, the capsules were filled with lactose.

starch composition	working conditions (°C) T_b, T_m, T_e, T_n, $\frac{L}{D}$ LFV	disintegration property of the capsules
maize starch (about 20% amylose)	110, 120, 140, 140, 66, 840	floculation in water of 36°C, disintegration within 30 minutes
maize starch (65% amylose) 80% b.w., water 20% b.w.	110, 120, 140, 140, 66, 840	no opening in water of 36° C within 30 minutes
maize starch (0% amylose, 100% amylopectin) 79.2 b.w., water 20.8% b.w.	110, 120, 140, 140, 66, 836	disintegration in water of 36°C, disintegration within 30 minutes

This invention has been described in terms of specific embodiments set forth in detail, but it should be understood that these are by way of illustration only and that the invention is not necessarily limited thereto. Modifications and variations will be apparent from this disclosure and may be resorted to without departing from the spirit of this invention, as those skilled in the art will readily understand. Accordingly, such variations and modifications of the disclosed invention are considered to be within the purview and scope of this invention and the following claims.

CLAIMS for the designated states BE, CH, DE, FR, GB, IT, LI, LU, NL, SE:

1. A composition for use in a moulding apparatus, which composition comprises starch, or a starch related material, having a molecular mass range of from 10,000 to 20,000,000 Dalton and a water content range of, preferably, from 5 to 30% by weight of the dry composition.

2. A composition according to Claim 1, wherein the starch comprises in the range from 0 to 100%, preferably 0 to 70%, by weight of amylose, and in the range from 100 to 0%, preferably 95 to 10%, by weight of amylo-pectin.

3. A composition according to Claim 1 or 2, wherein the starch is mixed with one or more plasticizers, at a preferred concentration in the range of from 0.5 to 40% based upon the weight of the starch, wherein the one or more plasticizer may be chosen from the following:

polyethylene glycol and low-molecular-weight organic plasticizers (for example glycerol, sorbitol, dioctylsodium sulphosuccinate, triethyl citrate, tributyl citrate, 1,2 propylenglycol, mono-, di- and tri-acetates of glycerol).

4. A composition according to Claim 1, 2 or 3, wherein the starch is mixed with one or more lubricant at a preferred concentration in the range of from 0.001 to 10% based upon the weight of the starch, wherein the one or more lubricant may be chosen from the following:

lipids, for example, glycerides;

wax and phospholipids;

unsaturated and saturated plant fatty acids and salts thereof;

stearates of aluminium, calcium, magnesium and tin; and

talc and silicones.

5. A composition according to Claim 1, 2, 3 or 4, wherein the starch is mixed with one or more colouring agent, at a preferred concentration in the range of from 0.001 to 10% based upon the weight of the starch, wherein the one or more colourant may be chosen from the following:

azo-dyes and other dyestuffs and pigments (for example iron oxides, titanium dioxides, and natural dyes).

6. A composition according to any preceding claim, wherein the starch is chosen from one or more of the following:

corn wheat starch, pototo starch, rice starch and tapioca starch, preferably corn wheat starch and potato starch.

7. A composition according to any preceding claim, wherein the starch or a further starch is chosen from one or more of the following:

a starch treated with a cross-linking agent or by a cross-linking method;

a starch which has been chemically modified, (for example, oxidised starch, starch monophosphate, starch diphosphate, starch acetate, starch sulphate, starch hydroxyethylether, carboxymethyl starch, starch ether, 2-hydroxypropyl starch, alphatized starch, starch xanthide, starch chloroacetic acid, starch ester, formaldehyde starch, and sodium carboxymethyl starch); or

a starch which has been modified by prior processing (for example, by treatment with an acid and/or an enzyme in order to yield dextrines; and/or pregelatinizing; and/or treatment with ultrasonic radiation; and/or treatment with gamma radiation).

8. A composition according to any preceding claim, wherein the starch is mixed with one

or more extender chosen from the following group which comprises:

modified or treated starches as described in Claim 7, sunflower proteins, soybean proteins, cotton seed proteins, peanut proteins, rape seed proteins; blood proteins, egg proteins, and acetylated derivates thereof, water soluble derivates of cellulose (for example hydroxypropyl cellulose, hydroxyethylcellulose, hydroxypropyl methylcellulose, hydroxypropylmethylcellulose, and sodium carboxy methylcellulose); polyvinylpyrrolidone; bentonite, polyvinylacetate-phtalate; vinylacetate, gelatin; monosaccharides, oligosaccharides (for example lactose), polysaccharides (for example agar-agar, alginates and alginic acids, gum arabic, guar, and dextran); crosslinked gelatin, polysaccharides (for example cellulose, methylcellulose, chitin, polymaltose, polyfructose), pectine, silicates, carbonates and bicarbonates.

9. A composition according to any preceding claim, wherein the starch is mixed with one or more polymer having enteric properties, which polymer is chosen from the following group which comprises:

hydroxypropylmethylcellulosephtalate (HPMCP), celluloseacetylphtalate (CAP), acrylates and methacrylates, polyvinyl-acetatephtalate (PVAP), phthalated gelatin, succinated gelatin, crotonic acid, and shellac.

10. A capsule formed from a composition or from a foam described in any one of the preceding claims.

11. A product formed from a composition or from a foam thereof described in any preceding claim, wherein the product may be:

a candy, a packaging container for packaging,

for example, food stuffs, pharmaceuticals, chemicals, dyestuffs, spices, fertilizing combinations, seeds, cosmetics and agricultural products;

matrices of various shapes and sizes which may comprise substances and/or active ingredients (for example, food-stuffs, pharmaceuticals, chemicals, dyestuffs, spices, fertilizing combinations, seeds, cosmetics and agricultural products) which are microdispersed within the matrix and released from it through disintegration and/or dissolution and/or bioerrosion and/or diffusion depnding on the solubility characteristics of the used starch composition, and sometimes resulting in a controlled release delivery system for the microdispersed substance; and

medical and surgery products.

12. A pharmaceutical, whenever microdispersed within a matrix starch composition as described in Claim 11.

13. A method for injection moulding a product, which method comprises the steps of:

maintaining a starch composition as described in any one of Claims 1 to 9, under controlled conditions of temperature, pressure and water content;

plasticizing the starch composition, preferably at a temperature in the range from 80-240°C;

injecting a sufficient amount of the plasticized composition into a mould, wherein the injection pressure is preferably in the range from 600×10^5 to $3000 \times 10^5 N/m^2$;

cooling the injected plasticized composition in the mould; and

ejecting the moulded product from the mould.

14. A method according to Claim 13, wherein the operating pressure is in the range from 600×10^5 to 3000×10^5 N/m^2.

15. A method according to Claim 13 or 14, wherein the composition is heated until it passes through the glass transition range.

16. A method according to Claim 13, 14 or 15, wherein the plasticized starch composition is moulded at a temperature below 80°C.

17. A product whenever prepared by a process as described in any one of Claims 13 to 16.

18. A method according to any one of Claims 13 to 16, wherein the product is a capsule part.

19. A capsule part whenever prepared by the process of claim 18.

CLAIMS for the designated state AT:

1. A process for producing a composition for use in a moulding apparatus, which process comprises formulating a starch, or a starch related material, having a molecular mass range of from 10,000 to 20,000,000 Dalton and a water content range of, preferably, from 5 to 30% by weight of the dry composition.

2. A process according to Claim 1, wherein the starch comprises in the range from 0 to 100%, preferably 0 to 70%, by weight of amylose, and in the range from 100 to 0%, preferably 95 to 10%, by weight of amylo-pectin.

3. A process according to Claim 1 or 2, wherein the starch is mixed with one or more plasticizers, at a preferred concentration in the range of from 0.5 to 40% based upon the weight of the starch, wherein the one or more plasticizer may be chosen from the following:

polyethylene glycol and low-molecular-weight organic plasticizers (for example glycerol, sorbitol, dioctylsodium sulphosuccinate, triethyl citrate, tributyl citrate, 1,2 propylenglycol, mono-, di- and tri-acetates of glycerol).

4. A process according to Claim 1, 2 or 3, wherein the starch is mixed with one or more lubricant at a preferred concentration in the range of from 0.001 to 10% based upon the weight of the starch, wherein the one or more lubricant may be chosen from the following:

lipids, for example, glycerides;

wax and phospholipids;

unsaturated and saturated plant fatty acids and salts thereof;

stearates of aluminium, calcium, magnesium and tin; and

talc and silicones.

5. A process according to Claim 1, 2, 3 or 4, wherein the starch is mixed with one or more colouring agent, at a preferred concentration in the range of from 0.001 to 10% based upon the weight of the starch, wherein the one or more colourant may be chosen from the following:

azo-dyes and other dyestuffs and pigments (for example iron oxides, titanium dioxides, and natural dyes).

6. A process according to any preceding claim, wherein the starch is chosen from one or more of the following:

corn wheat starch, pototo starch, rice starch and tapioca starch, preferably corn wheat starch and potato starch.

7. A process according to any preceding claim, wherein the starch or a further starch is chosen from one or more of the following:

a starch treated with a cross-linking agent or by a cross-linking method;

a starch which has been chemically modified, (for example, oxidised starch, starch monophosphate, starch diphosphate, starch acetate, starch sulphate, starch hydroxyethylether, carboxymethyl starch, starch ether, 2-hydroxypropyl starch, alphatized starch, starch xanthide, starch chloroacetic acid, starch ester, formaldehyde starch, and sodium carboxymethyl starch); or

a starch which has been modified by prior processing (for example, by treatment with an acid and/or an enzyme in order to yield dextrines; and/or pregelatinizing; and/or treatment with ultrasonic radiation; and/or treatment with gamma radiation).

8. A process according to any preceding claim, wherein the starch is mixed with one

or more extender chosen from the following group which comprises:

modified or treated starches as described in Claim 7, sunflower proteins, soybean proteins, cotton seed proteins, peanut proteins, rape seed proteins; blood proteins, egg proteins, and acetylated derivates thereof, water soluble derivates of cellulose (for example hydroxypropyl cellulose, hydroxyethylcellulose, hydroxypropyl methylcellulose, hydroxypropylmethylcellulose, and sodium carboxy methylcellulose); polyvinyl-pyrrolidone; bentonite, polyvinylacetate-phtalate; vinylacetate, gelatin; monosaccharides, oligosaccharides (for example lactose), poly-saccharides (for example agar-agar, alginates and alginic acids, gum arabic, guar, and dextran); crosslinked gelatin, polysaccharides (for example cellulose, methylcellulose, chitin, polymaltose, polyfructose), pectine, silicates, carbonates and bicarbonates.

9. A process according to any preceding claim, wherein the starch is mixed with one or more polymer having enteric properties, which polymer is chosen from the following group which comprises:

hydroxypropylmethylcellulosephtalate (HPMCP), celluloseacetylphtalate (CAP), acrylates and methacrylates, polyvinyl-acetatephtalate (PVAP), phthalated gelatin, succinated gelatin, crotonic acid, and shellac.

10. A process wherein a capsule is produced from a composition or from a foam thereof produced by a process described in any one of the preceding claims.

11. A process wherein a product is produced from a composition or from a foam thereof produced by a process described in any one of claims

1 to 9, wherein the product may be:

a candy, a packaging container for packaging, for example, food stuffs, pharmaceuticals, chemicals, dyestuffs, spices, fertilizing combinations, seeds, cosmetics and agricultural products;

matrices of various shapes and sizes which may comprise substances and/or active ingredients (for example, food-stuffs, pharmaceuticals, chemicals, dyestuffs, spices, fertilizing combinations, seeds, cosmetics and agricultural products) which are microdispersed within the matrix and released from it through disintegration and/or dissolution and/or bioerrosion and/or diffusion depnding on the solubility characteristics of the used starch composition, and sometimes resulting in a controlled release delivery system for the microdispersed substance; and

medical and surgery products.

12. A process for producing a pharmaceutical, wherein the pharmaceutical is microdispersed within a matrix starch composition prepared by a process as described in Claim 11.

13. A method for injection moulding a product, which method comprises the steps of:

maintaining a starch composition, produced by a process as described in any one of claims 1 to 9, under controlled conditions of temperature, pressure and water content;

plasticizing the starch composition, preferably at a temperature in the range from 80-240°C;

injecting a sufficient amount of the plasticized composition into a mould, wherein the injection pressure is preferably in the range from 600 $\times 10^5$ to $3000 \times 10^5 N/m^2$;

cooling the injected plasticized composition in the mould; and

ejecting the moulded product from the mould.

14. A method according to Claim 13, wherein the operating pressure is in the range from 600×10^5 to 3000×10^5 N/m^2.

15. A method according to Claim 13 or 14, wherein the composition is heated until it passes through the glass transition range.

16. A method according to Claim 13, 14 or 15, wherein the plasticized starch composition is moulded at a temperature below 80°C.

17. A method according to any one of Claims 13 to 16, wherein the product produced is a capsule part.

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Date: 24th February 1984

Our Ref: HL 27998/000/MRJ/DAN/MM

Dear Sirs,

Re: European Patent Application No. 84300940.8 :
WARNER-LAMBERT COMPANY

We request that the following mistake in the description of the above-mentioned application be corrected as indicated.

In line 34 on page 13, the phrase "when the pressure" should read "when there is pressure".

A copy of the present letter is enclosed, which we request may be date-stamped and returned to us in the enclosed, addressed envelope by way of acknowledgement of the safe receipt of the present letter.

Yours faithfully,
HASELTINE LAKE & CO., by:

JONES, Michael Raymond

For the purpose of publication,
correction not allowed.
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A.J. COPINI - 3 JULI 1984

Empfang bestätigt
Receipt acknowledged
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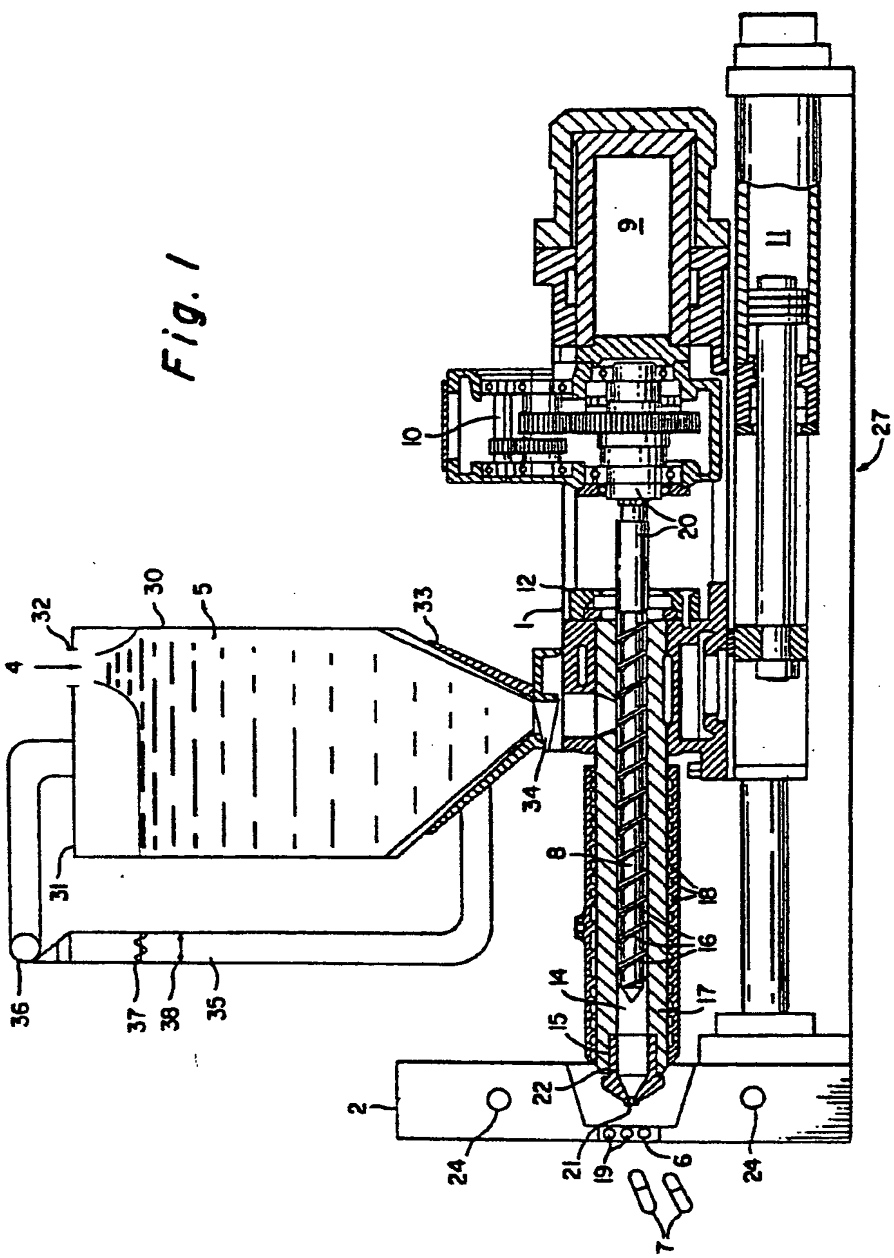
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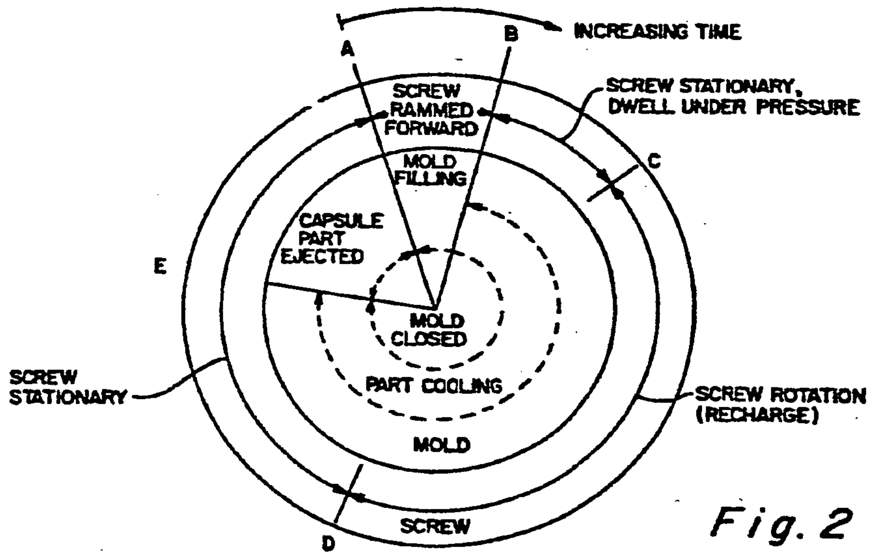
Fig. 1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B
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C
MOLD FILLING
CAPSULE PART EJECTED
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SCREW STATIONARY
PART COOLING
SCREW ROTATION (RECHARGE)
MOLD
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Fig. 2

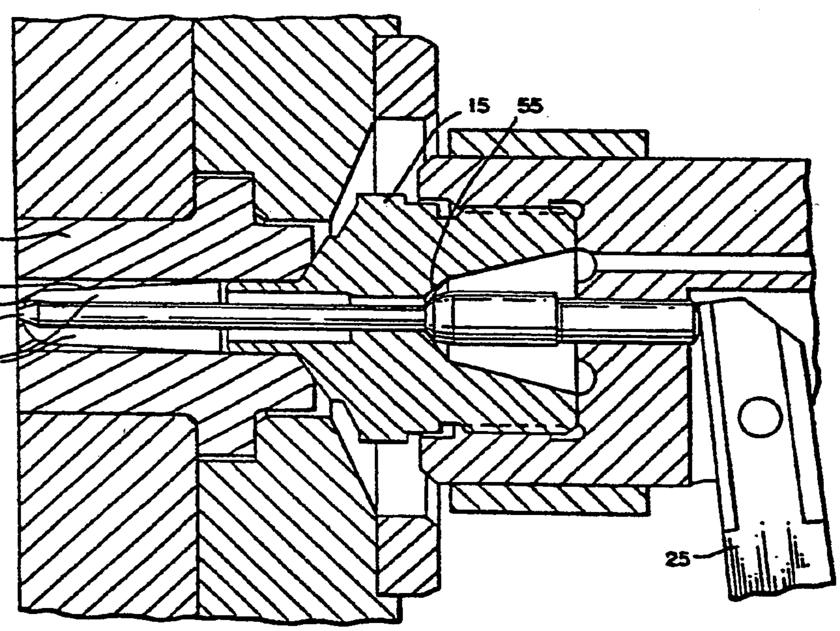
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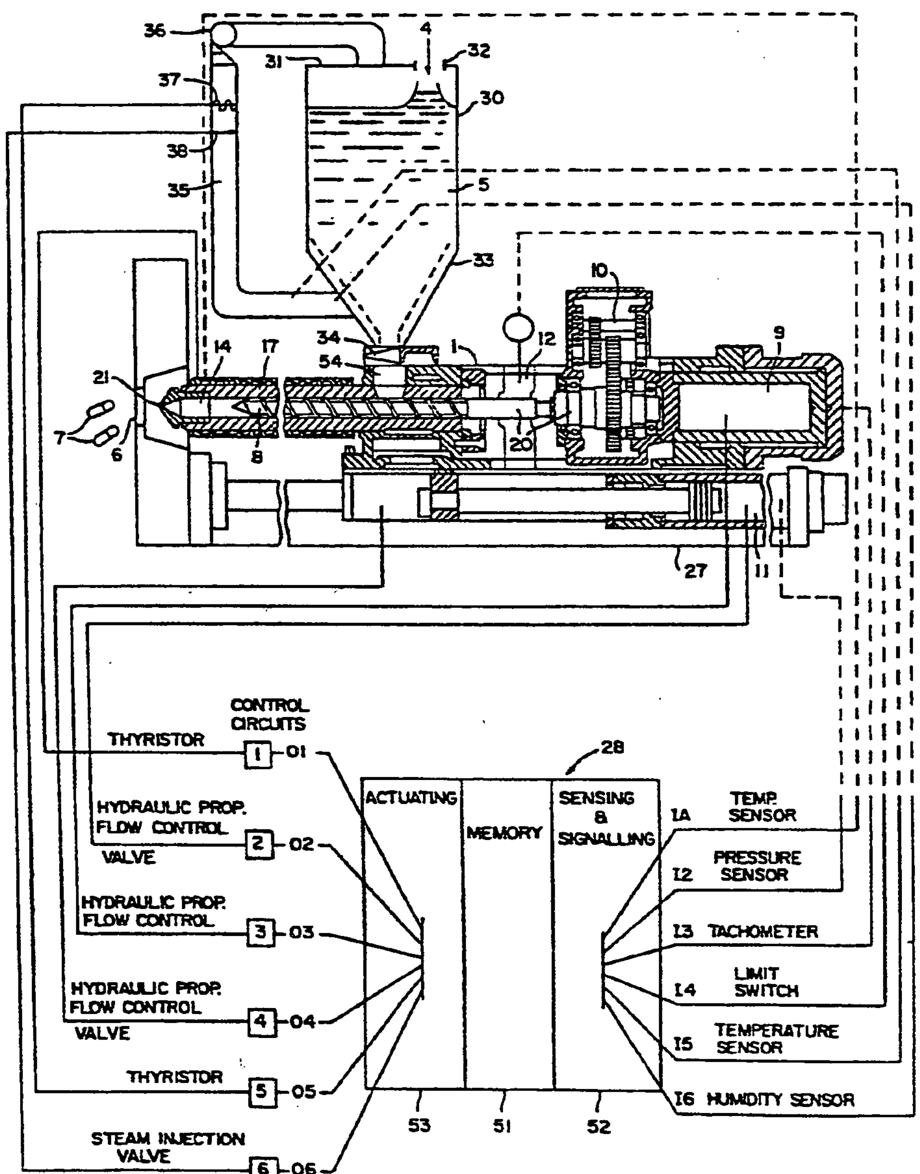
Fig. 4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CONTROL CIRCUITS
THYRISTOR
1
01
28
HYDRAULIC PROP. FLOW CONTROL VALVE
2
02
ACTUATING
MEMORY
SENSING & SIGNALLING
TEMP. SENSOR
IA
PRESSURE SENSOR
I2
HYDRAULIC PROP. FLOW CONTROL
3
03
I3 TACHOMETER
LIMIT SWITCH
I4
HYDRAULIC PROP. FLOW CONTROL VALVE
4
04
TEMPERATURE SENSOR
I5
THYRISTOR
5
05
I6 HUMIDITY SENSOR
53
51
52
STEAM INJECTION VALVE
6
06

Fig. 3

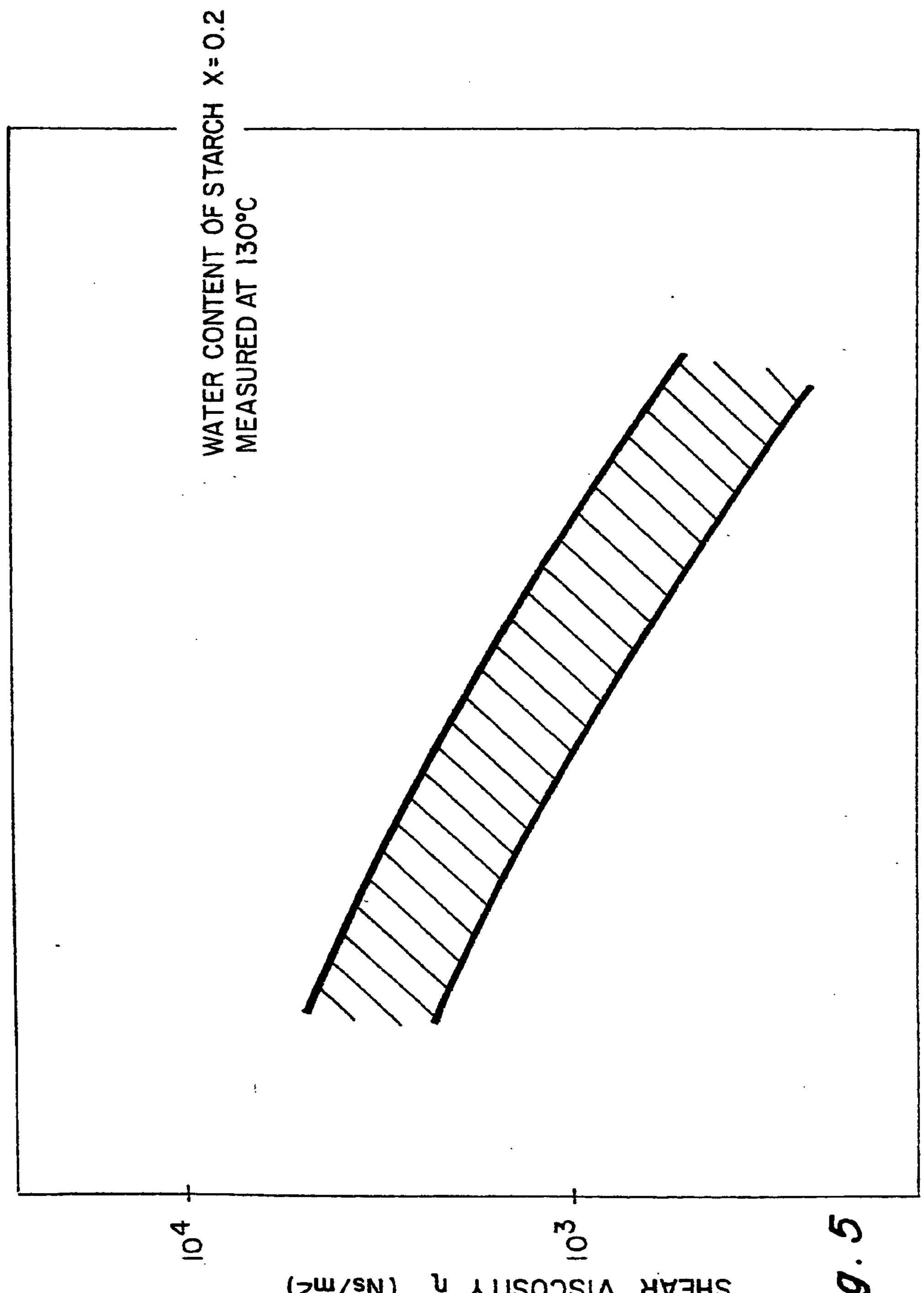
WATER CONTENT OF STARCH X=0.2
MEASURED AT 130°C
10^4
10^3
SHEAR VISCOSITY η (Ns/m²)

Fig. 5

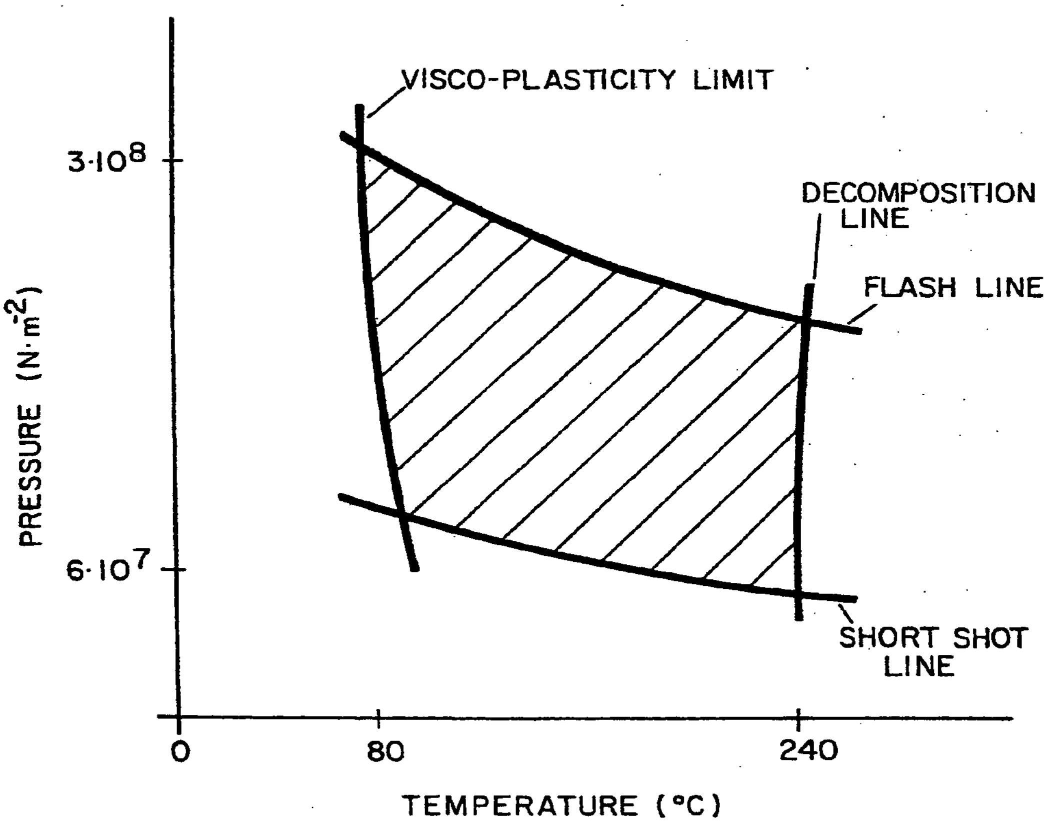
VISCO-PLASTICITY LIMIT
DECOMPOSITION LINE
FLASH LINE
SHORT SHOT LINE
3·10^8
6·10^7
PRESSURE (N·m^-2)
0
80
240
TEMPERATURE (°C)

Fig.6

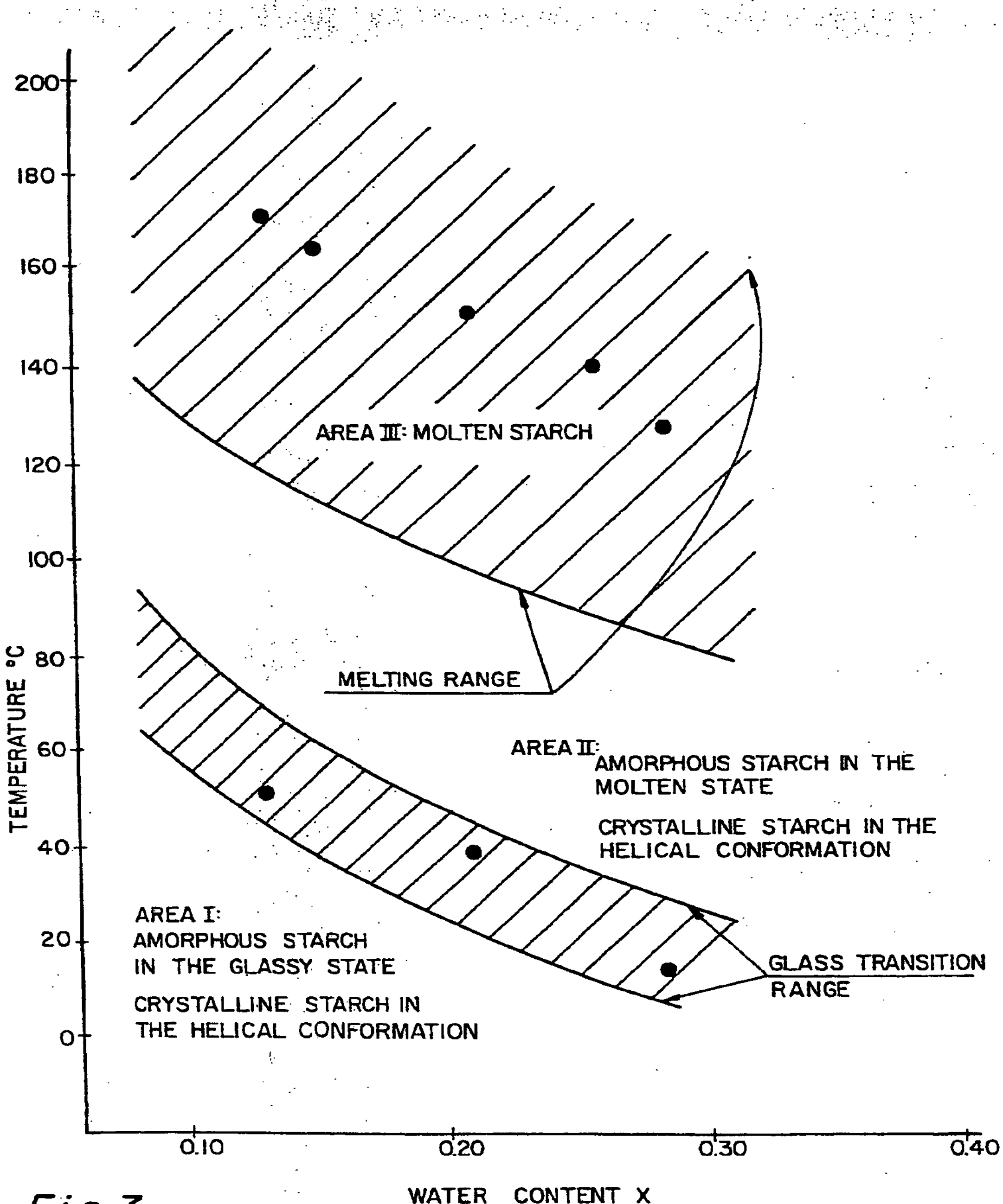
200
180
160
140
120
100
80
60
40
20
0
TEMPERATURE °C
AREA III: MOLTEN STARCH
MELTING RANGE
AREA II: AMORPHOUS STARCH IN THE MOLTEN STATE
CRYSTALLINE STARCH IN THE HELICAL CONFORMATION
AREA I: AMORPHOUS STARCH IN THE GLASSY STATE
CRYSTALLINE STARCH IN THE HELICAL CONFORMATION
GLASS TRANSITION RANGE
0.10
0.20
0.30
0.40
WATER CONTENT X

Fig.7

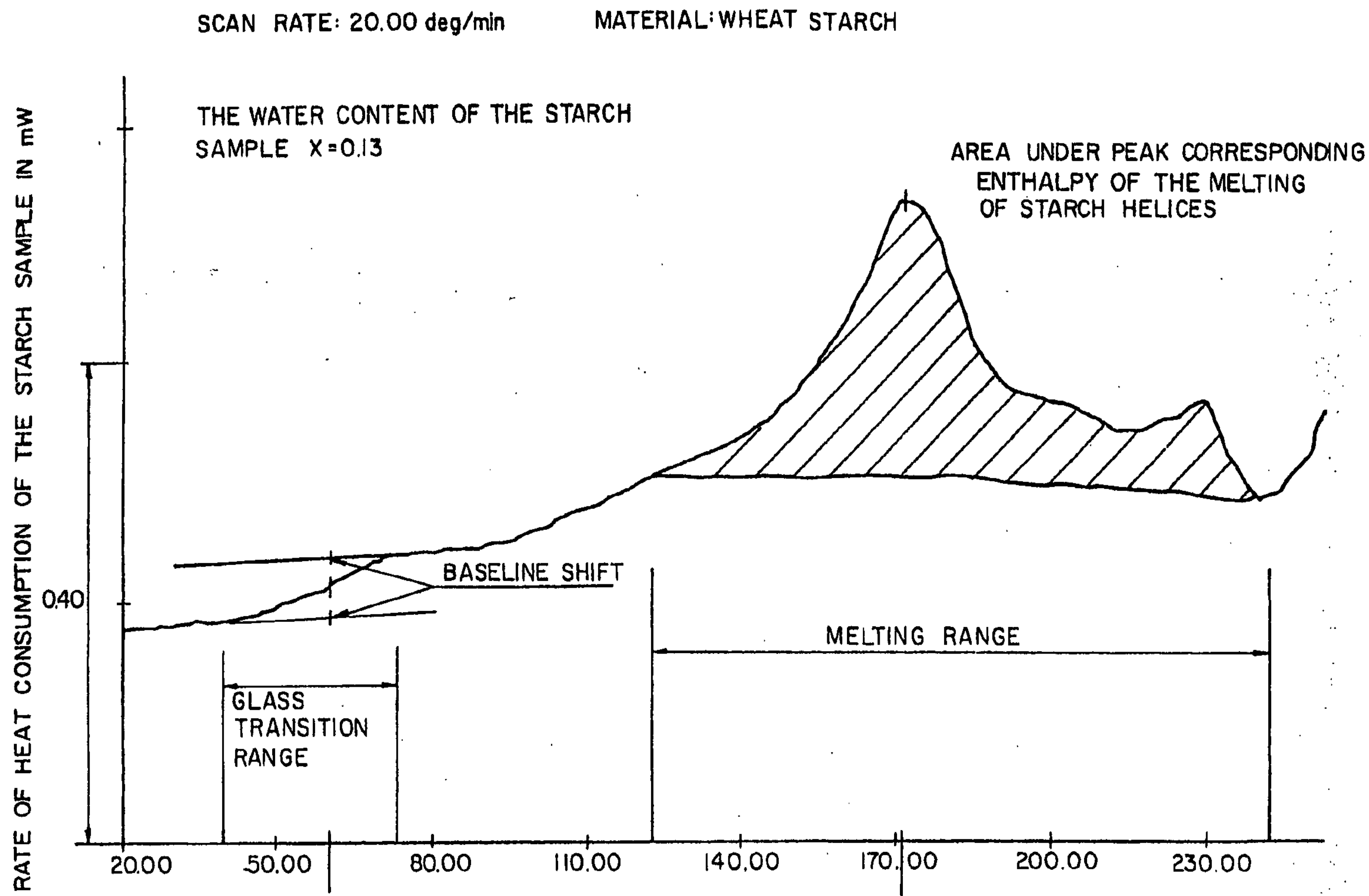
SCAN RATE: 20.00 deg/min
MATERIAL: WHEAT STARCH
THE WATER CONTENT OF THE STARCH
SAMPLE X=0.13
AREA UNDER PEAK CORRESPONDING
ENTHALPY OF THE MELTING
OF STARCH HELICES
BASELINE SHIFT
MELTING RANGE
GLASS
TRANSITION
RANGE
0.40
RATE OF HEAT CONSUMPTION OF THE STARCH SAMPLE IN mW
20.00
50.00
80.00
110.00
140.00
170.00
200.00
230.00
T_G
T_M
TEMPERATURE IN °C

Fig. 8

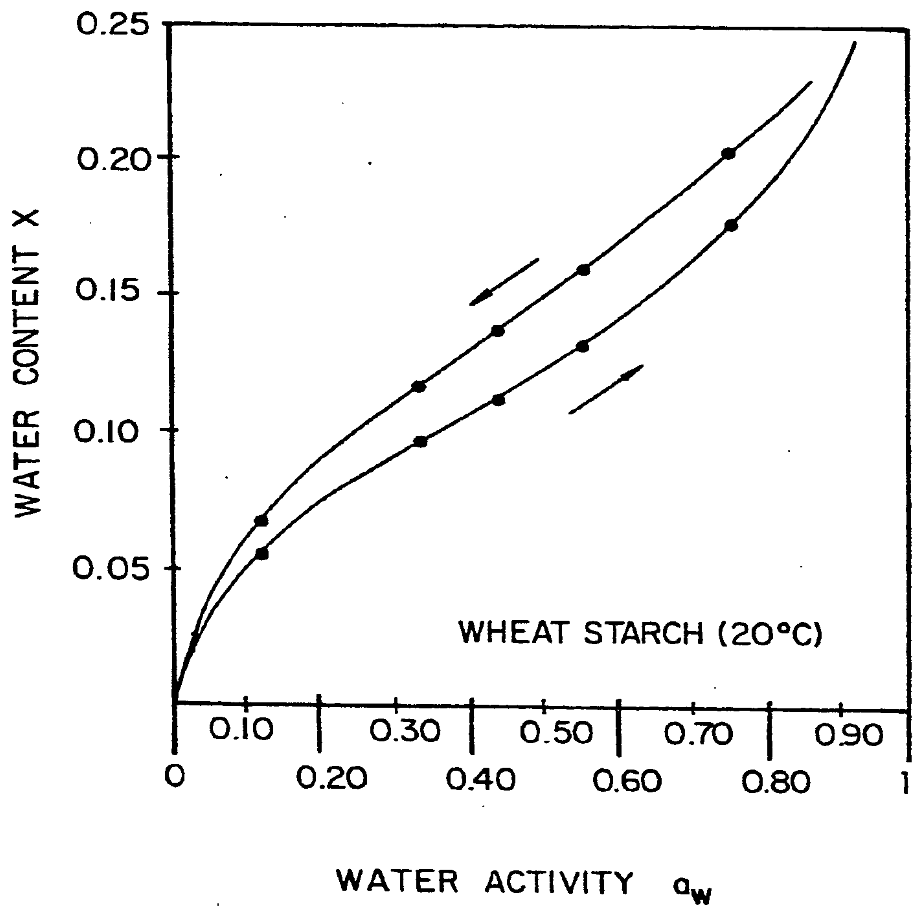
0.25
0.20
0.15
0.10
0.05
WATER CONTENT X
WHEAT STARCH (20°C)
0.10
0.30
0.50
0.70
0.90
0
0.20
0.40
0.60
0.80
1
WATER ACTIVITY a_w

Fig. 9